

PATENT ABSTRACTS OF JAPAN

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(54) PRODUCTION OF HYDROGEN BY THERMOCHEMICAL DECOMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To high efficiently and selectively take out hydrogen as thermodynamic chemical equilibrium is kept by allowing a material containing carbon such as an organic material to react with supercritical water in the presence of a material absorbing carbon dioxide in the quantity enough to absorb all generated carbon dioxide.

SOLUTION: A material containing carbon such as coal, petroleum, plastic, biomass is reacted with supercritical water under ≥ 220 atm at $\geq 600^{\circ}$ C, preferably under 250-600 atm at 650-800 $^{\circ}$ C. As a result, the oxidation is performed with dissolved oxygen without adding an oxidizing agent. The equilibrium reaction of a gas produced by the reaction of the organic material with supercritical water is expressed by a formula, $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$. The reaction proceeds by taking out CO_2 as a carbonate in the presence of the material absorbing CO_2 such as CaO , MgO and an oxidizing acid. In such a case, the presence of the sufficient quantity of a material for taking out sulfur, halogen or the like as a water soluble salt, such as NaOH , Na_2CO_3 , KOH , K_2CO_3 , is preferable.

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of hydrogen of performing thermochemical decomposition, without making the matter containing carbon reacting with supercritical water, being the approach of returning supercritical water and making hydrogen generating, and making it existing in the amount system of reaction which can absorb all the carbon dioxides that generated the carbon-dioxide absorbing material at least, and adding a parenchyma top oxidizer on conditions with a 220 or more atmospheric-pressures temperature [of pressures] of 600 degrees C or more.

[Claim 2] The manufacture approach of the hydrogen which supplied the matter and carbon-dioxide absorbing material containing carbon to the system of reaction, and was indicated by claim 1 which takes out hydrogen and a carbonate from the system of reaction.

[Claim 3] The manufacture approach of the hydrogen indicated by claim 1 or claim 2 which decomposes a carbonate thermally, changes into a carbon-dioxide absorbing material, and is again returned to the system of reaction.

[Claim 4] The manufacture approach of the hydrogen indicated by one of either claim 1 using CaO, MgO, or an iron oxide as matter which absorbs a carbon dioxide thru/or the claims 3.

[Claim 5] The manufacture approach of hydrogen that the matter containing carbon was indicated by one of claims 1 thru/or claims 4 which is coal, petroleum, plastics, biomass, any one **, or two or more.

[Claim 6] The manufacture approach of the hydrogen indicated by one of either claim 1 whose reaction temperature is 650 degrees C - 800 degrees C thru/or the claims 5.

[Claim 7] The manufacture approach of the hydrogen indicated by one of either claim 1 made to exist in the amount system of reaction which absorbs all of sulfur, a halogen, and the sulfur which generated at least the matter which forms a water-soluble salt and a halogen with a carbon-dioxide absorbing material thru/or the claims 6.

[Claim 8] as the matter which forms sulfur, a halogen, and a water-soluble salt -- NaOH and Na₂CO₃ -- the manufacture approach of the hydrogen indicated by one of either claim 1 using one sort of the compound chosen from the group which consists of CO₃, KOH, and K₂CO₃, or two sorts or more thru/or the claims 7.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] The hydrogen manufacture approach of pyrolyzing the organic substance, such as coal and petroleum, with elevated-temperature high pressure, and manufacturing hydrogen gas, the manufacture approach of the hydrogen from water gas, the manufacture approach of the hydrogen which electrolyzes water, etc. are learned from the former. The place by which this invention belongs to the technical field which manufactures such hydrogen, and it is characterized [the] uses the heat generated in case the carbon in the organic substance is oxidized, and is related with the approach of disassembling supercritical water thermochemically and manufacturing hydrogen alternatively.

[0002]

[Description of the Prior Art] Although there are some processes which disassemble and gasify the organic substance, such as coal, petroleum, plastics, and biomass, most oxidative degradation methods are used. Since catabolic rate is high, the oxidative degradation method for using supercritical water also in an oxidative degradation method is used well recently. The oxidative degradation method of the organic substance for having used conventional supercritical water for drawing 1 is shown. It is mixed with water, and after the organic substance is fed with a pump 2 by the reactor 1 with which water will be in a supercritical condition and secures fixed time amount reaction time within a reactor with a temperature of about 400 degrees C, it is divided into the gas oxidative degradation product which cooled and decompressed and was generated with the condensator 3, water, and solid-state residue. At this time, when air or oxygen is separately supplied to a reactor 3 as an oxidizer and the heat to generate runs short, a supercritical condition is maintained by applying heat from the exterior. In such an operating condition, the nitrogen gas with which the gas oxidative degradation product was generated from the nitrogen content in a carbon dioxide and the organic substance occupies most. In the case of the gas pyrolysate and many which use a carbon monoxide, a carbon dioxide, a low-grade hydrocarbon, hydrogen, and nitrogen as a principal component in this case, a liquefied product is obtained although there is also the decomposing method only the heat from the outside performs a pyrolysis at the temperature of 400-600 degrees C supercritical underwater, without adding an oxidizer. The yield of hydrogen is low, although the yield of gas becomes high so that it pyrolyzes at an elevated temperature. Returning supercritical water and taking out hydrogen using the carbon in the organic substance, although research was variously done about disassembling the organic substance by supercritical underwater and conventionally taking out the gas of the organic substance origin was not noted, and it was not considered. this invention person used to find out that what is necessary is just to combine the supercritical water and the carbon-dioxide absorbing material of specific conditions, without adding a parenchyma top oxidizer, as a result of narrowing [a lifting and] down a target to the ability of supercritical water to be returned efficiently and studying thermochemical disassembly of water wholeheartedly how from such a viewpoint.

[0003]

[Problem(s) to be Solved by the Invention] When disassembling the organic substance, without

adding an oxidizer with the water of a supercritical condition, in the reaction temperature of about 400 degrees C, the gas which the pyrolysis of the organic substance is not carried out completely, but uses a carbon monoxide, a carbon dioxide, hydrogen, nitrogen, a low-grade hydrocarbon, etc. as a principal component, and a liquefied product are generated. There are very few rates of the hydrogen generated at this time. If reaction temperature is raised at 650 more degrees C, a liquefied product will disappear and the organic substance will be gasified completely. However, the presentation of generation gas uses a carbon monoxide, a carbon dioxide, and hydrogen as a principal component, the presentation stops at the thermodynamical equilibrium value determined with reaction temperature and reaction pressure, and the rate of hydrogen gas becomes about 30%. This invention succeeds in raising the rate of the hydrogen in generation gas by leaps and bounds, maintaining this thermodynamic chemical equilibrium using the supercritical water and the generating gas absorption matter of specific conditions. Furthermore, it found that it is finally also recoverable as a water-soluble salt, without catching sulfur and a halogen with a reactor and making them shift into the gas to generate. In this invention, the semantics of not adding a parenchyma top oxidizer also means that it is not necessary to remove specially the air which faces loading a reactor with others, a sample, or a raw material, and is included in a sample thru/or a raw material. [semantics / that it is not necessary to add an oxidizer] Since this does not need to send in air with high pressure, it also becomes reduction of compression power and leads also to the advantage which does not require the operating cost of the whole equipment.

[0004]

[Means for Solving the Problem] In the 650-degree C pyrolysis of the organic substance supercritical underwater [above-mentioned], the rate of the hydrogen in gas does not become high, because the carbon monoxide in the gas formed at the reaction of the organic substance and the water of a supercritical condition, a steam, a carbon dioxide, and hydrogen are in chemical equilibrium. Static reaction $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ (1)

It is described by *****. The operation which reacts with a carbon dioxide on condition that the temperature of a reactor and a pressure here, and is fixed as a solid-state is carried out, and if the matter (carbon-dioxide absorbing material) which does not affect this chemical equilibrium relation at all is made to live together at a reaction place superfluously beforehand in itself, the amount of the carbon dioxide in gas will decrease by the reaction with this matter.

[0005] In order to maintain the above-mentioned chemical equilibrium relation to the amount of this carbon dioxide that decreased in number, a reaction advances in the direction which generates CO_2 and H_2 by the reaction of CO and H_2O inevitably. Produced CO_2 reacts with a carbon-dioxide absorbent, and is removed from gas. As a result, finally, it becomes chemical equilibrium into gas in the form where a carbon monoxide, a carbon dioxide, and a lot of steams and hydrogen of ***** small quantity exist. Gas and a solid-state (mixture of the solid matter which absorbed the ash content, the unreacted diacid carbonizing absorbent, and carbon dioxide in the organic substance, and was produced) become possible [dissociating, since a steam returns to water by cooling]. It becomes possible to manufacture the gas which uses hydrogen as a principal component from the organic substance as a result. It is a reaction formula if a carbon-dioxide absorbent is now set to X. $\text{C} + 2\text{H}_2\text{O} + \text{X} = (\text{XCO}_2) + 2\text{H}_2$ (2)

It can come out and describe. The hydrogen gas to generate can make water the origin, it can be shown that the above-mentioned generalization reaction formula manufactures hydrogen alternatively from the carbon and water in the organic substance, and this can be regarded as the thermochemical decomposition reaction of water.

[0006] Although such [naturally] heat can also be used since heat of reaction is emitted when the carbon-dioxide absorbing material, for example, CaO etc., added to the system of reaction besides the heat of combustion generated in case the carbon which the organic substance holds as a heat source which drives a reaction is oxidized reacts with water and it is set to calcium $(\text{OH})_2$, when it runs short, (2) types can be advanced by applying heat from the exterior. When Matter X is used as a carbon-dioxide absorbent $\text{X} + \text{CO}_2 = \text{XCO}_2$ (3),

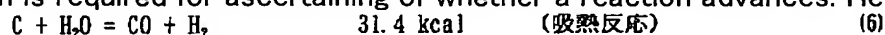
In order to produce ***** it must be beyond the temperature that becomes settled thermodynamically. Therefore, the temperature of the system of reaction of this invention turns

into beyond the temperature that the above-mentioned reaction formula (3) produces inevitably. as a carbon-dioxide absorbent, metallic oxides, such as CaO, MgO, and an iron oxide (FeO, Fe 2O3, Fe3O4), and the hydroxide (calcium -- (OH)2 -- two -- Mg -- (OH)2 -- two -- Fe -- (OH)2 -- two -- Fe -- (OH)2 -- three -- a grade) of a metal of the same kind are typical. Since it is economical, CaO and calcium (OH)2 are the matter recommended most. Moreover, although not mentioned as an example, MgO and Mg (OH)2, FeO, Fe 2O3, and Fe3O4 are checking the effective thing. A hydroxide is dehydration at hot conditions. calcium (OH)2=CaO+H2O (4)

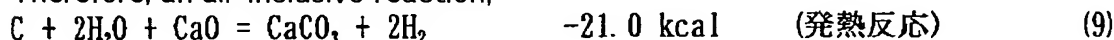
Mg (OH) 2=MgO+H2O (5)

The case where a metallic oxide of the same kind is added from the beginning by that of *****, and a reaction place become equal. The sulfur content in the organic substance generates [in water] a poorly soluble sulfate in this case and is not desirable, although it reacts with X and is fixed as a sulfate in the above-mentioned reaction process. In order to prevent this, H2S once produced in gasification apart from X and the matter Y which is easy to react are added, and the matter water-soluble at the reaction of Y and H2S is made to form.

[0007] Consequently, since the sulfur in the organic substance serves as water solubility, the ash content in the carbon-dioxide absorbing material and the unreacted carbon-dioxide absorbing material after a reaction, and the organic substance etc. is separable from other solid-states. It is fixable as a water-soluble salt similarly about a halogen. as Matter Y -- NaOH and Na2 -- there are CO3, KOH, and K2CO3. Moreover, in many cases, since Matter Y acts as a catalyst which promotes the reaction of the organic substance and the water of a supercritical condition, it is convenient. Moreover, although the case where Na2CO3 was used as an example was shown, it is checking that NaOH, KOH, and K2CO3 also carry out the same operation. A thermodynamic examination is required for ascertaining of whether a reaction advances. Heat of



Therefore, an all-inclusive reaction,



It is net exothermic reaction at least, and has expected a next door and going on spontaneously thermodynamically.

[0008]

[Embodiment of the Invention] The gestalt of operation of this invention is as follows.

(1) The manufacture approach of hydrogen of performing thermochemical decomposition, without making the matter containing carbon reacting with supercritical water, being the approach of returning supercritical water and making hydrogen generating, and making it existing in the amount system of reaction which can absorb all the carbon dioxides that generated the carbon-dioxide absorbing material at least, and adding a parenchyma top oxidizer on conditions with a 220 or more atmospheric-pressures temperature [of pressures] of 600 degrees C or more.

(2) The manufacture approach of the hydrogen which supplied the matter and carbon-dioxide absorbing material containing carbon to the system of reaction, and was generated, and the hydrogen indicated by claim 1 which takes out a carbonate from the system of reaction.

(3) The manufacture approach of the hydrogen indicated by claim 1 or claim 2 which decomposes a carbonate thermally, changes into a carbon-dioxide absorbing material, and is again returned to the system of reaction.

(4) The manufacture approach of the hydrogen indicated by one of either claim 1 using CaO, MgO, or an iron oxide (FeO, Fe 2O3, Fe3O4) as matter which absorbs a carbon dioxide thru/or the claims 3.

(5) The manufacture approach of hydrogen that the matter containing carbon was indicated by one one of claims 1 thru/or claims 4 which is coal, petroleum, plastics, biomass, any one **, or two or more.

(6) The manufacture approach of the hydrogen indicated by one of either claim 1 whose reaction temperature is 650 degrees C – 800 degrees C thru/or the claims 5.

(7) The manufacture approach of the hydrogen indicated by one of either claim 1 whose pressures are 250 thru/or 600 atmospheric pressures thru/or the claims 6.

(8) The manufacture approach of the hydrogen indicated by one of either claim 1 made to exist in the amount system of reaction which absorbs all of sulfur, a halogen, and the sulfur which generated at least the matter which forms a water-soluble salt and a halogen with a carbon-dioxide absorbing material thru/or the claims 6.

(9) as the matter which forms sulfur, a halogen, and a water-soluble salt -- NaOH and Na₂ -- the manufacture approach of the hydrogen indicated by one of either claim 1 using one sort of the compound chosen from the group which consists of CO₃, KOH, and K₂CO₃, or two sorts or more thru/or the claims 7.

[0009]

[Explanation of concrete implementation of invention] It carried out using the micro autoclave 5 with an outer diameter of 30mm which has the capillary tube 7 shown in drawing 2. The pressure in a micro autoclave was changed by adjusting the volume and heating temperature of the amount of pure water with which it is filled up in early stages. Reaction pressure was calculated with the equation of state of water.

[0010]

[Equation 1]

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

p: pressure R:gas constant T:absolute-temperature V_m: -- the volume a which water occupies, and b: -- a constant [0011]

[Example 1] 4.0 cc of pure water of the amount of conventions is mixed with 0.1g (76% of carbon contents) of Pacific Ocean charcoal and 0.6g of calcium(OH)₂ powder of the superfluous equivalent ground in the reaction container 6, and it poured into the reaction container 6 with a bore of 12mm with the syringe, heat tracing of it was carried out with the electric furnace, and it was made to react for 20 minutes with 1000 atmospheric pressures of 650 degrees C from the capillary tube 7 with an aperture of 1.6mm. While cooling after the reaction, collecting the gas which occurred in the sampling bag and measuring generating capacity, the presentation was measured by the gas chromatograph. The solid-state and liquid inside a reactor analyzed by collecting.

[0012]

[Example 2] 0.1g of sodium carbonates was added to the sample, and also the same actuation was repeated on the same conditions as an example 1.

[Example 3] The pressure was changed to 300 atmospheric pressures, having used as one cc the amount of the pure water which fills up 0.03g with the Pacific Ocean charcoal, and is filled up with 0.2g and Na₂CO₃ for calcium (OH)₂ 0.03g and the first stage, and also the same actuation as an example 1 was repeated.

[Example 4] The pressure was changed to 250 atmospheric pressures, having used as 0.55 cc the amount of the pure water which fills up 0.025 with the Pacific Ocean charcoal and is filled up with 0.15g and Na₂CO₃ for calcium (OH)₂ 0.025g and the first stage, and also the same actuation as an example 1 was repeated. For the comparison, the sample which ground only coal was made and others repeated the same actuation as an example 1. Drawing 3 shows the result. The amount of the gas obtained even if it carries out pyrolysis processing by 1000 atmospheric pressures and 650-degree C supercritical underwater does not pass [g] only over coal and water in 0.7l. /, and the rate of hydrogen is also as low as 48%. The rate of hydrogen becomes 78% while generation capacity will increase by 2.5 times, if calcium (OH)₂ which is a diacid carbonizing absorbent is added to this system of reaction. Furthermore, if Na₂CO₃ is added, generation capacity will increase further. This drawing shows that Na₂CO₃ has a function as a catalyst which raises the reaction rate of a reaction formula (2). Of course, sulfur is caught by addition of Na₂CO₃ as water-soluble salts. Although the capacity which will be generated if

reaction pressure is lowered decreases, the rate of the hydrogen in gas is still high, and is only judged that it is that the reaction rate only fell. Drawing 3 is drawing having shown the concrete result, and is also the proof which proves work of the additive in this invention to coincidence. If reservation of a heat source is possible as mentioned above, since two-mol hydrogen is manufactured from one mol of carbon, in the case of coal (76% of carbon contents), the hydrogen of 2.83Nm³/kg can manufacture theoretically from (9) types. From the result of an experiment, CH₄ other than hydrogen of a some carries out a byproduction. This is considered to be generated by the reaction of CO₂ and H₂. Since S minutes in coal are nonaqueous solubility although fixed as CaSO₄ when not adding Na₂CO₃, the separation from other solid matter is difficult. However, by adding Na₂CO₃, finally S in coal is caught as water-soluble Na₂SO₄, and since it can extract out of a system by water treatment, it becomes advantageous.

[0013]

[Examples 5-8] Four kinds of coal system organic substance of the dry distillation object of the Australia YARUN charcoal (brown coal), the Pacific Ocean charcoal (bituminous coal), the Australia BUREA SOL charcoal (bituminous coal), and BUREA SOL charcoal in this sequence Make 0.1g into a sample, respectively and to this calcium (OH)₂ which is a carbon-dioxide absorbing material 0.6g, 0.1g of Na₂CO₃ was mixed as a sulfur content scavenger which served water as the catalyst of four cc and a reaction, heat tracing was carried out with the electric furnace, and it was made to react on the reaction temperature of 650 degrees C, pressure 1000 atmospheric pressure, and the conditions for reaction-time 20 minutes. This example is considered that the same result is obtained also by the same pressure as the example shown in drawing 3 although pressures are 1000 atmospheric pressures and a high case. While cooling after the reaction, collecting the gas which occurred in the sampling bag and measuring generating capacity, the presentation was measured by the gas chromatograph. The solid-state and liquid inside a reactor analyzed by collecting. Drawing 4 shows an amount and a presentation of as opposed to 1g of carbon in a sample for the gas which occurred then. In addition, it is the amount of hydrogen in four sorts of coal system organic substance, and the Pacific Ocean charcoal which was shown in the middle in front Naka, and it is shown for a comparison of the amount of hydrogen when this is all emitted. Except for the dry distillation object of BUREA SOL charcoal, the hydrogen almost near the amount of theory was generated. Also to the dry distillation object of BUREA SOL charcoal, if reaction time is secured enough, the same result will be obtained. In the case of Pacific Ocean charcoal, it was shown, but since the amount of hydrogen generation which exceeds the amount of hydrogen generation calculated from the hydrogen content in the Pacific Ocean charcoal you to be Haruka is obtained, the hydrogen shown by drawing 4 is judged to be that by which the water supplied as a reaction raw material was converted into hydrogen by the reaction formula (2). Moreover, in generation gas, the matter which has the origin in the sulfur contained in coal is not detected, but sulfur is judged to be what was fixed as a solid-state or water-soluble matter.

[0014]

[Examples 9-12] a tree -- waste -- a polyvinyl chloride -- polyethylene -- black -- rubber -- four -- a kind -- the organic substance -- this -- sequence -- respectively -- 0.1 -- g -- a sample -- ** -- carrying out -- this -- a carbon dioxide -- an absorbing material -- it is -- calcium -- (-- OH --) -- two -- 0.6 -- g -- water -- four -- cc -- and -- a reaction -- a catalyst -- having served -- a sulfur content -- a scavenger -- ***** -- Na -- two -- CO -- three -- 0.1 -- g -- mixing -- an electric furnace -- heat tracing -- carrying out -- reaction temperature -- 650 -- degree C -- a pressure -- 1000 -- an atmospheric pressure -- reaction time -- 20 -- a minute -- conditions -- reacting -- having made . While cooling after the reaction, collecting the gas which occurred in the sampling bag and measuring generating capacity, the presentation was measured by the gas chromatograph. The solid-state and liquid inside a reactor analyzed by collecting. Drawing 5 shows the amount of the gas which occurred then, and a presentation. Drawing 5 shows the experimental result at the time of applying this approach to the organic substance other than coal. He can understand that all the matter containing the carbon content which can burn as the organic substance can be set as the object of this approach.

[0015]

[Application in the process of an example] The process shown in drawing 6 based on the result of examples 1-12 was possible. although many kinds of configurations are possible as a process -- this time -- as the basic plan of a process design -- (1) -- all required heat energy is provided with the coal which is a raw material.

(2) The heating method of a raw material adopts an internal heating method with high effectiveness. That is, coal slurry is heated using the heat of reaction of CaO.

It adopted. Under this concept, the conversion of C in injection coal will keep high a part for C in the solid rather picked out from a presser-foot reactor low, will decompose CaCO_3 and calcium $(\text{OH})_2$ with the heat which converts C into CO_2 with air with a CaO regenerator (combustor of unburnt carbon) separately, and generates this in that case, and will reproduce them to CaO. In this case, CO_2 concentration in exhaust gas becomes about 25%. This is recoverable as the CaO regenerator, then CO_2 of about 100% of high concentration of a heat tracing method. This means that the carbon dioxides produced using coal can be collected by high concentration, and means that special concentration separation actuation is unnecessary. It becomes advantageous also from a viewpoint of greenhouse-gases discharge control. The material balance in the case of carrying out 1 t/hr processing of the coal from an experimental result and the heat balance were calculated. 50% of 1t of supplied coal reacts, and 1400Nm of the hydrogen and methane of 3 are generated. The carbon content which remained is burned with air or oxygen with a regenerator, and reproduces CaCO_3 and calcium $(\text{OH})_2$ to CaO with the heat. Since the heat of the equivalent occurs in case CaO is mixed with H_2O , most heat of combustion which coal finally has will be used for gas generation, and can attain high cold gas efficiency (ratio of the heat of combustion which the generated gas holds, and the heat of combustion which the supplied coal holds). When the heat needed with this regenerator is securable separately, generation capacity can be made to increase by gathering the conversion of a reactor.

[0016]

[Effect of the Invention] In this invention, it is characteristic for this approach to be able to be large also to the organic substance other than coal, and to be able to be adapted for it. The height of this flexibility also deserves attention. This process is roughly classified according to a raw material system as follows.

(1) In process process, the thing which use as a raw material process (4) biomass which uses as a raw material the process (3) plastics which use as a raw material the process (2) heavy oil which uses coal as a raw material, reduced pressure residual oil, etc. and for which a process is constructed to each raw material of a certain thing is possible for some difference, and it is efficient, and hydrogen is manufactured and it can prevent the discharge to the environment of a harmful element. Hydrogen can be thought by both sides of an energy recovery and matter recovery. Moreover, collecting by high concentration is also possible, CO_2 which carries out a byproduction is very advantageous also from a viewpoint of processing of CO_2 which is global warming gases, and use, and there is also little impact given to an environment. The technique which can be manufactured can be alternatively offered for hydrogen only in the combination of the heat-source matter of carbon content, such as coal, petroleum, biomass, and plastics, and cheap and common matter called water, air, a limestone, and a sodium carbonate. As concrete effectiveness, the load to an environment is not given but (1) fossil fuel resource (especially coal) and biomass can be changed into clean hydrogen energy. Various development of the approach of hydrogen being efficient as energy and using it is carried out, and, as a result, prolongation-of-life-ization of a fossil fuel resource can be performed.

(2) Even when moisture, such as brown coal, is included so much, it becomes possible to use as it is, without making it dry like the former.

(3) It is possible to catch the matter leading to environmental pollution, such as sulfur in the carbon content matter and chlorine, etc.

(4) plastics -- not a form but the hydrogen of heat energy -- conversion -- possible -- an energy recovery and matter recycle -- correspondence to both of the methods is possible.

There are no generating of dioxin and generating of a hydrogen chloride which pose a problem by incineration. **** is mentioned.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The explanatory view having shown an example using the supercritical water by the conventional technique of the pyrolysis oxidation process of the organic substance

[Drawing 2] The sectional view of the equipment used for operation of this invention

[Drawing 3] The explanatory view showing the experimental result and the effectiveness of a catalyst of checking radical Motohara ** of this invention

[Drawing 4] The explanatory view showing the experimental result about the capacity generated at the reaction with the supercritical water of the various coal in the conditions of this invention, and its presentation

[Drawing 5] The explanatory view showing the experimental result about the capacity generated at the reaction with the supercritical water of the various organic substance other than ** and the coal in the conditions of this invention, and its presentation

[Drawing 6] The flow chart explanatory view having shown an example of the hydrogen manufacture process from the organic substance based on this invention

[Description of Notations]

1 --- Supercritical water reactor

2 --- Pump

3 --- Condensator

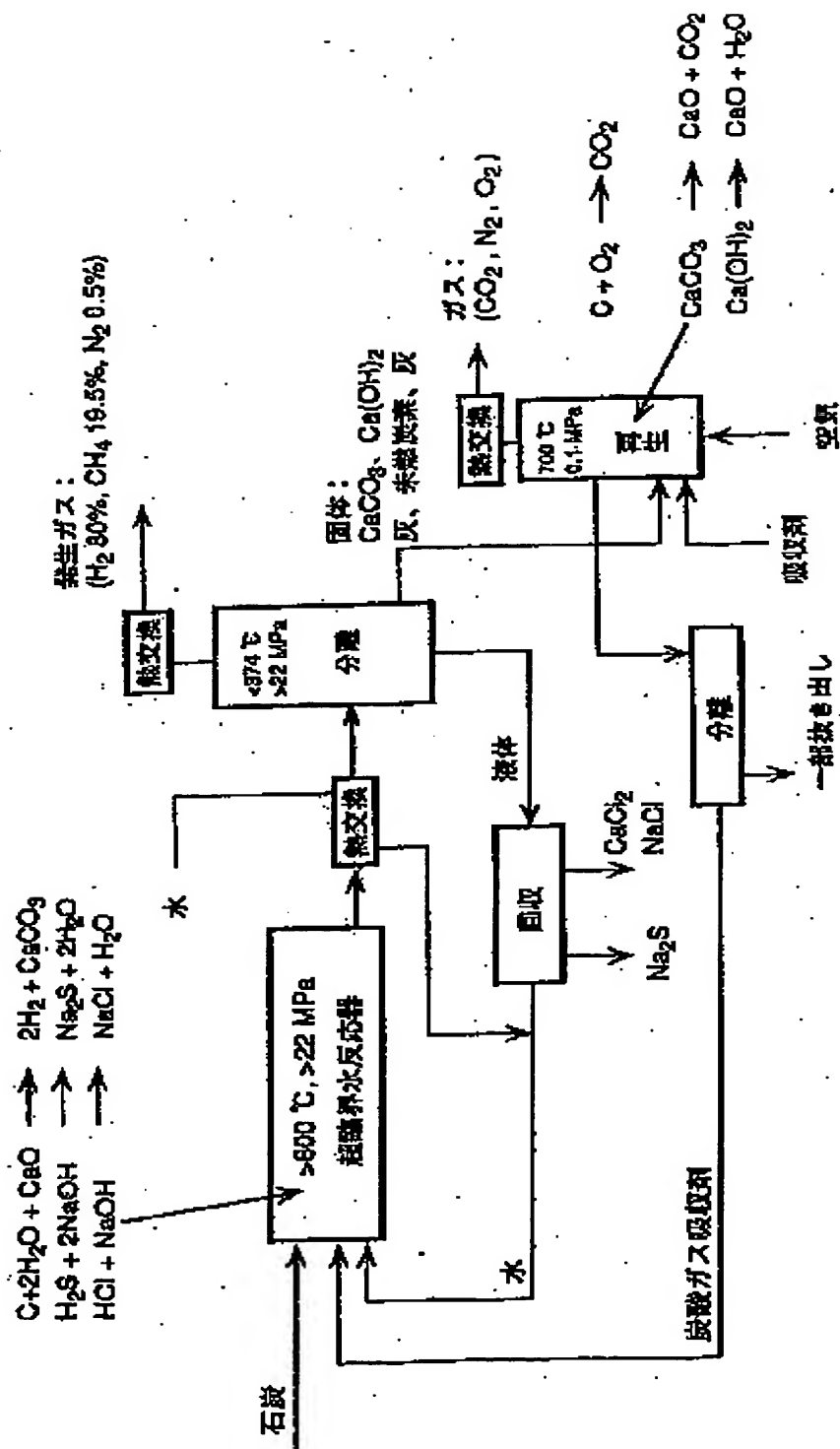
4 --- Gas eliminator

5 --- Micro autoclave

6 --- Reaction section

7 --- Capillary tube

[Translation done.]



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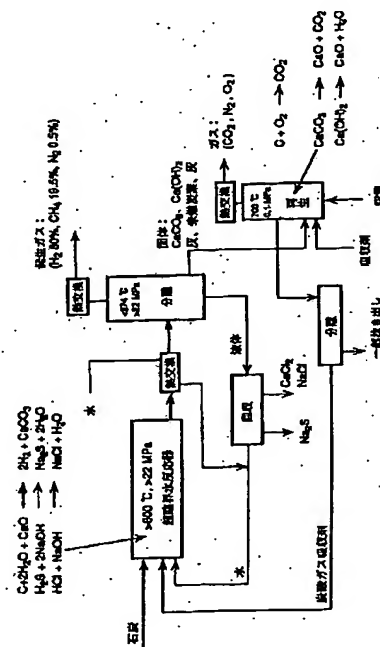
最終頁に続く

(54) 【発明の名称】 熱化学的分解による水素の製造方法

(57) 【要約】

【課題】 石炭、石油、プラスチック、バイオマス等の有機物を超臨界水を用いて分解するに際して、水素を選択的に取り出す。

【解決手段】 実質上酸化剤を加えずに、温度と圧力を特定した超臨界水のもとで、二酸化炭素を吸収する物質を存在、少なくとも発生する二酸化炭素をすべて吸収できる量存在させることにより、熱化学反応が促進され、超臨界水が還元され、水素が選択的に取り出せる。



【特許請求の範囲】

【請求項1】 炭素を含有する物質を超臨界水と反応させ、超臨界水を還元して水素を生成させる方法であって、二酸化炭素吸収物質を、少なくとも生成したすべての二酸化炭素を吸収できる量反応系に存在させ、かつ、圧力220気圧以上温度600℃以上の条件で実質上酸化剤を加えることなく熱化学的分解を行う水素の製造方法。

【請求項2】 炭素を含有する物質と二酸化炭素吸収物質を反応系に供給し、水素と炭酸塩を反応系から取り出す請求項1に記載された水素の製造方法。

【請求項3】 炭酸塩を加熱分解し、二酸化炭素吸収物質に変え、再び反応系に戻す請求項1または請求項2に記載された水素の製造方法。

【請求項4】 二酸化炭素を吸収する物質としてCaO、MgOまたは酸化鉄を用いる請求項1ないし請求項3のいずれかの一つに記載された水素の製造方法。

【請求項5】 炭素を含有する物質が、石炭、石油、プラスチック、バイオマス、のいずれか一つ、または二つ以上である請求項1ないし請求項4のいずれかの一つに記載された水素の製造方法。

【請求項6】 反応温度が650℃～800℃である請求項1ないし請求項5のいずれかの一つに記載された水素の製造方法。

【請求項7】 二酸化炭素吸収物質と共に、硫黄やハロゲンと水溶性の塩を形成する物質を、少なくとも生成した硫黄やハロゲンをすべて吸収する量反応系に存在させる請求項1ないし請求項6のいずれかの一つに記載された水素の製造方法。

【請求項8】 硫黄やハロゲンと水溶性の塩を形成する物質として、NaOH、Na₂CO₃と、KOH、K₂CO₃からなる群より選ばれる化合物の1種または2種以上を用いる請求項1ないし請求項7のいずれかの一つに記載された水素の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 石炭や石油などの有機物を高温高压で熱分解し水素ガスを製造する水素製造方法や、水性ガスからの水素の製造方法、水を電気分解する水素の製造方法等は、従来から知られている。本発明は、このような水素を製造する技術分野に属し、その特徴とするところは、有機物中の炭素を酸化する際に発生する熱を利用し、超臨界水を熱化学的に分解し水素を選択的に製造する方法に関するものである。

【0002】

【従来の技術】 石炭、石油、プラスチック、バイオマス、等の有機物を分解してガス化するプロセスは幾つかあるが、酸化分解法が最も多く利用されている。酸化分解法の中でも超臨界水を利用する酸化分解法は分解速度が高いので最近よく利用される。図1に従来の超臨界

水を利用した有機物の酸化分解法を示す。有機物は水と混合され、水が超臨界状態となる反応装置1にポンプ2で圧送され400℃程度の温度の反応器内での一定時間反応時間を確保した後、冷却器3で冷却され、減圧され生成したガス状の酸化分解生成物、水、固体残渣に分離される。このとき、酸化剤として空気または酸素を別途反応器3に供給し、発生する熱が不足する場合には外部から熱を加えることにより超臨界状態を維持する。この様な操作条件では、ガス状の酸化分解生成物は二酸化炭素と有機物中の窒素分から生成された窒素ガスが大部分を占めている。酸化剤を加えずに外部からの熱のみで400～600℃の温度で熱分解を超臨界水中で行う分解法もあるが、この場合は一酸化炭素、二酸化炭素、低級炭化水素、水素、窒素を主成分とするガス状の熱分解生成物と多くの場合液状の生成物が得られる。高温で熱分解するほどガスの収率は高くなるが、水素の収率は低い。従来は、有機物を超臨界水中で分解して、有機物由来のガスを取り出すことに関して、いろいろ研究が行われていたが、有機物中の炭素を用いて、超臨界水を還元して水素を取り出すことは、着目されていなかったし、考えられたこともなかった。本発明者は、このような観点から、いかに水の熱化学的分解を起こし、効率よく超臨界水を還元できるかに的を絞って、鋭意研究した結果、実質上酸化剤を加えることなく、特定条件の超臨界水と二酸化炭素吸収物質を組み合わせれば良いことを見出したものである。

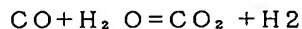
【0003】

【発明が解決しようとする課題】 有機物を超臨界状態の水で酸化剤を加えずに分解する場合、400℃程度の反応温度では有機物は完全には熱分解されず一酸化炭素、二酸化炭素、水素、窒素、低級炭化水素等を主成分とするガスと液状の生成物が生成される。この時生成する水素の割合は非常に少ない。反応温度をさらに650℃に上昇させると液状生成物は消滅し有機物は完全にガス化される。しかし、生成ガスの組成は、一酸化炭素、二酸化炭素、水素を主成分とするもので、その組成は反応温度と反応圧力により決定される熱力学的平衡値に留まり、水素ガスの割合は30%程度になる。本発明は、特定条件の超臨界水と発生ガス吸収物質を用い、この熱力学的化学平衡を維持したまま、生成ガス中の水素の割合を飛躍的に高めることに成功したものである。さらに、硫黄やハロゲンを反応器で捕捉し、生成するガス中に移行させることなく、最終的に水溶性の塩として回収することも見出した。本発明において、実質上酸化剤を加えないという意味は、酸化剤を加える必要がないという意味のほか、試料ないし原料を反応装置に装填するに際して、試料ないし原料の中に含まれる空気等をわざわざ除く必要はないという意味でもある。このことは、空気を高压で送り込む必要がないので、圧縮動力の削減にもなり、装置全体の運転費用がかからない利点にもつなが

る。

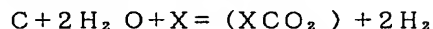
【0004】

【課題を解決する手段】上述の超臨界水中での有機物の650℃での熱分解においてもガス中の水素の割合が高*



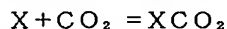
の関係で記述される。ここで反応器の温度、圧力の条件で二酸化炭素と反応し固体として固定する作用をし、それ自身はこの化学平衡関係になんら影響を与えない物質(二酸化炭素吸収物質)を予め過剰に反応場に共存させれば、ガス中の二酸化炭素の量はこの物質との反応により減少する。

【0005】この減少した二酸化炭素の量に対し前述の化学平衡関係を維持するためには、必然的にCOとH₂Oとの反応によりCO₂とH₂を生成する方向に反応が進行する。生じたCO₂は二酸化炭素吸収剤と反応し、※

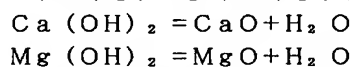


で記述できる。生成する水素ガスは水を起源とするもので、上記の総括反応式は有機物中の炭素と水から選択的に水素を製造することを示し、これは水の熱化学的分解反応と見ることができる。

【0006】反応を駆動する熱源としては有機物の保有する炭素を酸化する際に発生する燃焼熱のほか、反応系★

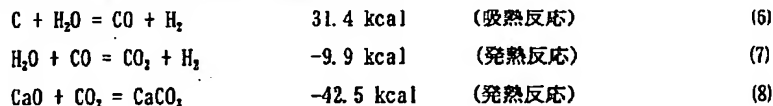


の反応を生じるためには、熱力学的に定まる温度以上でなければならない。したがって、本発明の反応系の温度は必然的に上記反応式(3)の生じる温度以上となる。二酸化炭素吸収剤としてはCaO、MgO、酸化鉄(FeO、Fe₂O₃、Fe₃O₄)等の金属酸化物及び同種金属の水酸化物(Ca(OH)₂、Mg(OH)₂、☆



を生じるので、同種金属酸化物を最初から加えた場合と反応場は等しくなる。有機物中の硫黄分は上記の反応過程でXと反応して硫酸塩として固定されるが、この場合水に難溶性の硫酸塩を生成してしまい好ましくない。これを防ぐため、Xとは別に一旦ガス化で生じるH₂Sと反応しやすい物質Yを加えYとH₂Sとの反応で水溶性の物質を形成させる。

【0007】この結果、有機物中の硫黄は水溶性となるため、反応後の二酸化炭素吸収物質や未反応の二酸化炭素吸収物質、有機物中の灰分等、他の固体から分離する◆



従って総括の反応は、



となり、少なくとも正味発熱反応であり、熱力学的には自発的に進行することが予想できた。

* ならないのは、有機物と超臨界状態の水との反応で形成されたガス中の一酸化炭素、水蒸気、二酸化炭素、水素が化学平衡にあるためである。平衡反応は、



※ ガスから除去される。この結果最終的にはガス中には極く少量の一酸化炭素と二酸化炭素および多量の水蒸気と水素が存在する形で化学平衡となる。ガスと固体(有機物中の灰分、未反応の二酸化炭素吸収剤および二酸化炭素を吸収して生じた固体物質の混合物)は冷却することにより水蒸気は水に戻るため分離することが可能となる。この結果有機物から水素を主成分とするガスを製造することが可能になる。今、二酸化炭素吸収剤をXとすると化学反応式は



★に加える二酸化炭素吸収物質例えばCaOなどは水と反応してCa(OH)₂になるとき反応熱を放出するから当然このような熱も利用することができるが、不足する場合は外部から熱を加えることにより(2)式を進行させることができる。物質Xを二酸化炭素吸収剤として用いる場合、



☆ Fe(OH)₂、Fe(OH)₃等が代表的なものである。経済的な理由からCaO、Ca(OH)₂が最も推奨される物質である。また、実施例としては挙げなかったが、MgO、Mg(OH)₂、FeO、Fe₂O₃、Fe₃O₄も有効であることを確認している。水酸化物は高温の条件では脱水反応



◆ ことができる。ハロゲンについても同様に水溶性の塩として固定可能である。物質Yとしては、NaOH、Na₂CO₃、KOH、K₂CO₃がある。また多くの場合物質Yは、有機物と超臨界状態の水との反応を促進する触媒として作用するので好都合である。また、実施例としてはNa₂CO₃を用いた場合を示したが、NaOH、KOH、K₂CO₃も同様の作用をすることを確認している。反応が進行するかどうかの見極めには熱力学的な検討が必要である。主反応の反応熱は

【0008】

50 【発明の実施の形態】本発明の実施の形態は以下のとお

りである。

(1) 炭素を含有する物質を超臨界水と反応させ、超臨界水を還元して水素を生成させる方法であって、二酸化炭素吸収物質を、少なくとも生成したすべての二酸化炭素を吸収できる量反応系に存在させ、かつ、圧力220気圧以上温度600℃以上の条件で実質上酸化剤を加えることなく熱化学的分解を行う水素の製造方法。

(2) 炭素を含有する物質と二酸化炭素吸収物質を反応系に供給し、生成した水素と炭酸塩を反応系から取り出す請求項1に記載された水素の製造方法。

(3) 炭酸塩を加熱分解し、二酸化炭素吸収物質に変え、再び反応系に戻す請求項1または請求項2に記載された水素の製造方法。

(4) 二酸化炭素を吸収する物質としてCaO、MgOまたは酸化鉄(FeO、Fe₂O₃、Fe₃O₄)を用いる請求項1ないし請求項3のいずれかの一つに記載された水素の製造方法。

(5) 炭素を含有する物質が、石炭、石油、プラスチック、バイオマス、のいずれか一つ、または二つ以上である請求項1ないし請求項4のいずれかの一つに記載された水素の製造方法。

(6) 反応温度が650℃～800℃である請求項1ないし請求項5のいずれかの一つに記載された水素の製造方法。

(7) 圧力が250乃至600気圧である請求項1ないし請求項6のいずれかの一つに記載された水素の製造方法。

(8) 二酸化炭素吸収物質と共に、硫黄やハロゲンと水溶性の塩を形成する物質を、少なくとも生成した硫黄やハロゲンをすべて吸収する量反応系に存在させる請求項1ないし請求項6のいずれかの一つに記載された水素の製造方法。

(9) 硫黄やハロゲンと水溶性の塩を形成する物質として、NaOH、Na₂CO₃、KOH、K₂CO₃からなる群より選ばれる化合物の1種または2種以上を用いる請求項1ないし請求項7のいずれかの一つに記載された水素の製造方法。

【0009】

【発明の具体的実施の説明】図2に示すキャピラリー7を有する外径30mmのマикроオートクレーブ5を用いて実施した。マクロオートクレーブ内の圧力は初期に充填する純水量の体積と加熱温度を調節することによって変化させた。反応圧力は水の状態方程式により計算した。

【0010】

【数1】

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

p：圧力

R：気体定数

T：絶対温度

V_m：水の占める体積

a, b：定数

【0011】

【実施例1】反応容器6内に粉碎した太平洋炭(炭素含有量76%)0.1gと過剰当量のCa(OH)₂粉末0.6gと規定量の純水4.0ccを混合し、口径1.6mmのキャピラリー7から、内径12mmの反応容器6に注射器で注入し、それを電気炉で外部加熱し、1000気圧650℃で20分間反応させた。反応後冷却し、発生したガスはサンプリングバッグに回収し発生ガス量を測定すると共に、組成はガスクロマトグラフにより測定した。反応器内部の固体と液体は回収し分析を行った。

【0012】

【実施例2】炭酸ナトリウム0.1gを試料に加えた他は実施例1と同じ条件で同じ操作を繰り返した。

【実施例3】太平洋炭を0.03g、Ca(OH)₂を0.2g、Na₂CO₃を0.03g、初期に充填する純水の量を1ccとして圧力を300気圧に変化させた他は実施例1と同じ操作を繰り返した。

【実施例4】太平洋炭を0.025g、Ca(OH)₂を0.15g、Na₂CO₃を0.025g、初期に充填する純水の量を0.55ccとして圧力を250気圧に変化させた他は実施例1と同じ操作を繰り返した。比較のために、石炭のみを粉碎した試料を作り、他は実施例1と同じ操作を繰り返した。図3は、その結果を示したものである。石炭と水のみを1000気圧、650℃の超臨界水中で熱分解処理をしても得られるガスの量は0.7リットル/gに過ぎず、また水素の割合も48%と低い。この反応系に二酸化炭素吸収剤であるCa(OH)₂を加えると生成ガス量が2.5倍に増加するとともに水素の割合が78%となる。さらに、Na₂CO₃を加えるとさらに生成ガス量が増加する。この図よりNa₂CO₃は反応式(2)の反応速度を向上させる触媒としての機能があることが分かる。もちろん、Na₂CO₃の添加により硫黄は水溶性の塩類として捕捉される。反応圧力を下げると生成するガス量は減少するが、ガス中の水素の割合は高いままであり、単に反応速度が低下しただけと判断される。図3は具体的結果を示した図であり、同時に本発明における添加剤の働きを証明する証拠でもある。前述のように熱源の確保が可能であれば、(9)式より、炭素1モルより2モルの水素が製造されるので、理論的には石炭(炭素分76%)の場合は、2.83Nm³/kgの水素が製造可能である。実験の結果からは水素の他に若干のCH₄が副生する。これはCO₂とH₂との反応により生じるものと考えられる。Na₂CO₃を加えない場合は石炭中のS分はCaSO₄として固定されるが非水溶性であるので他の固体物質からの分離は困難である。しかし、Na₂CO₃を

添加することにより、石炭中のSは最終的に水溶性の Na_2SO_4 として捕捉され、水処理により系外へ抜き出すことができるので有利になる。

【0013】

【実施例5～8】豪州ヤルーン炭（褐炭）、太平洋炭（瀝青炭）、豪州ブレアソール炭（瀝青炭）、ブレアソール炭の乾留物の4種類の石炭系有機物をこの順番で、それぞれ0.1gを試料とし、これに、二酸化炭素吸収物質である $\text{Ca}(\text{OH})_2$ を0.6g、水を4cc及び反応の触媒を兼ねた硫黄分捕捉剤として Na_2CO_3 を0.1g混合し、電気炉で外部加熱し、反応温度650℃、圧力1000気圧、反応時間20分の条件で反応させた。この実施例は圧力が1000気圧と高い場合であるが、図3に示した実施例と同様な圧力でも同様な結果が得られると考えられる。反応後冷却し、発生したガスはサンプリングバッグに回収し発生ガス量を測定すると共に、組成はガスクロマトグラフにより測定した。反応器内部の固体と液体は回収し分析を行った。図4は、そのとき発生したガスを試料中の炭素1gに対する量と組成を示したものである。なお、表中の真中に示したの

【0014】

【実施例9～12】木くず、ポリ塩化ビニル、ポリエチレン、黒ゴムの4種類の有機物をこの順番で、それぞれ0.1gを試料とし、これに、二酸化炭素吸収物質である $\text{Ca}(\text{OH})_2$ を0.6g、水を4cc及び反応の触媒を兼ねた硫黄分捕捉剤として Na_2CO_3 を0.1g混合し、電気炉で外部加熱し、反応温度650℃、圧力1000気圧、反応時間20分の条件で反応させた。反応後冷却し、発生したガスはサンプリングバッグに回収し発生ガス量を測定すると共に、組成はガスクロマトグラフにより測定した。反応器内部の固体と液体は回収し分析を行った。図5は、そのとき発生したガスの量と組成を示したものである。図5は、石炭以外の有機物に本方法を適用した場合の実験結果を示している。有機物としては燃焼可能な炭素分を含む物質は全て本方法の対象となり得ることが理解できよう。

【0015】

【実施例のプロセスへの適用】実施例1～12の結果を基に、図6に示すプロセスが可能であった。プロセスとしては何通りもの構成が可能であるが、今回はプロセス設計の基礎方針として、

(1) 必要な熱エネルギーは全て原料である石炭でまかなう。

(2) 原料の加熱方式は効率の高い内部加熱方式を採用する。すなわち、 CaO の反応熱を利用して石炭スラリーを加熱する。

を採用した。このコンセプトのもとでは、投入石炭中のCの反応率はむしろ低く押さえ反応器から取り出す固形物中のC分を高く保ちこれを別途 CaO 再生器（未燃カーボンの燃焼器）で空気によりCを CO_2 に転換しその際発生する熱で CaCO_3 、 $\text{Ca}(\text{OH})_2$ を分解し CaO に再生することになる。この場合は排ガス中の CO_2 濃度は25%程度となる。これを外部加熱方式の CaO 再生器とすれば100%近い高濃度の CO_2 として回収できる。これは石炭を利用して生じた二酸化炭素を高濃度で回収可能なことを意味し、特別な濃縮分離操作が不要なことを意味する。温暖化ガス排出抑制の観点からも、有利となる。実験結果から石炭を1t/h処理する場合の物質収支、熱収支を計算した。供給された石炭1tのうち50%が反応して1400Nm³の水素とメタンを生成する。残った炭素分は再生器で空気または酸素で燃焼させその熱で CaCO_3 と $\text{Ca}(\text{OH})_2$ を CaO に再生する。 CaO を H_2O と混合する際当量の熱が発生するので、最終的に石炭のもつ燃焼熱はほとんど、ガス生成に利用されることになり、高い冷ガス効率（生成したガスの保有する燃焼熱と投入した石炭の保有する燃焼熱の比）を達成できる。この再生器で必要とする熱を別途確保できる場合は、反応器の反応率を上げることにより生成ガス量を増加させることができる。

【0016】

【発明の効果】本発明において特徴的なのは本方法が石炭以外の有機物にも広く適応可能な点である。このフレキシビリティの高さも注目に値する。本プロセスは原料系によりおおまかに下記の様に分類される。

- (1) 石炭を原料とするプロセス
- (2) 重質油、減圧残油等を原料とするプロセス
- (3) プラスチック類を原料とするプロセス
- (4) バイオマスを原料とするプロセス

プロセス的には若干の相違はあるものの、それぞれの原料に対しプロセスを組むことが可能で、高効率で水素を製造し、かつ有害な元素の環境への排出を防止できる。水素はエネルギー回収と物質回収の両面で考えることが可能である。また、副生する CO_2 は高濃度で回収することも可能で地球温暖化ガスである CO_2 の処理、利用の観点からも非常に有利で、環境に与えるインパクトも少ない。石炭、石油、バイオマス、プラスチック、などの炭素含有の熱源物質と水、空気、石灰石、炭酸ナトリ

ウムという安価で一般的な物質の組み合わせのみで水素を選択的に製造可能な技術を提供することができる。具体的な効果としては、

(1) 化石燃料資源（特に石炭）、バイオマスを環境への負荷を与えず、クリーンな水素エネルギーに変換できる。水素はエネルギーとして高効率で使用方法が各種開発されており、この結果化石燃料資源の延命化ができる。

(2) 褐炭等水分を多量に含む場合でも、従来の様に乾燥せずにそのまま利用することが可能になる。

(3) 炭素含有物質中の硫黄、塩素等の環境汚染の原因となる物質などをも捕捉することが可能である。

(4) プラスチック類については熱エネルギーの形ではなく水素に転換可能で、エネルギー回収、物質リサイクルどちらの方式にも対応可能。焼却で問題となる、ダイオキシンの発生や塩化水素の発生がない。などが挙げられる。

【図面の簡単な説明】

【図1】従来技術による超臨界水を利用した有機物の熱分解酸化プロセスの一例を示した説明図

*【図2】本発明の実施に用いた装置の断面図

【図3】本発明の基本原理を確認する実験結果と触媒の効果を示す説明図

【図4】本発明の条件での各種石炭の超臨界水との反応で生成したガス量とその組成に関する実験結果を示す説明図

【図5】は、本発明の条件での石炭以外の各種有機物の超臨界水との反応で生成したガス量とその組成に関する実験結果を示す説明図

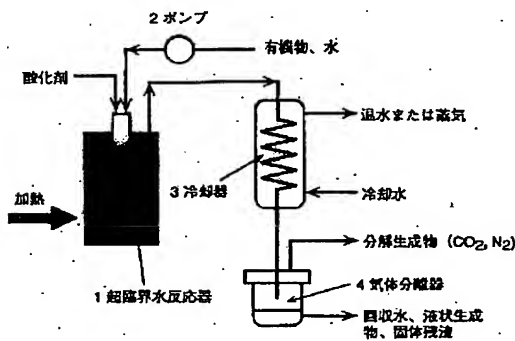
10 【図6】本発明に基づく有機物からの水素製造プロセスの一例を示したフローチャート説明図

【符号の説明】

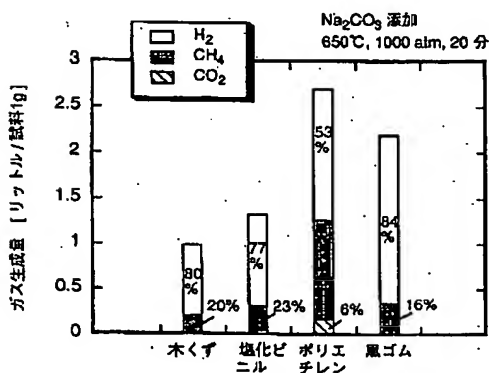
- 1…超臨界水反応装置
- 2…ポンプ
- 3…冷却器
- 4…気体分離器
- 5…マイクロオートクレーブ
- 6…反応部
- 7…キャピラリー

*20

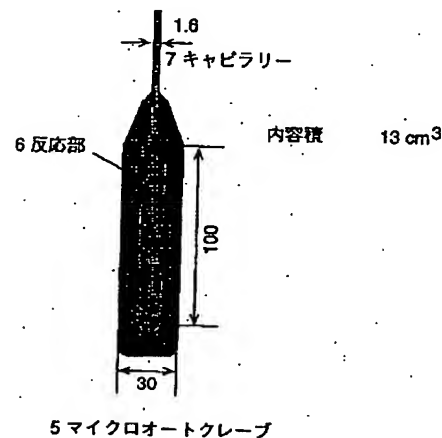
【図1】



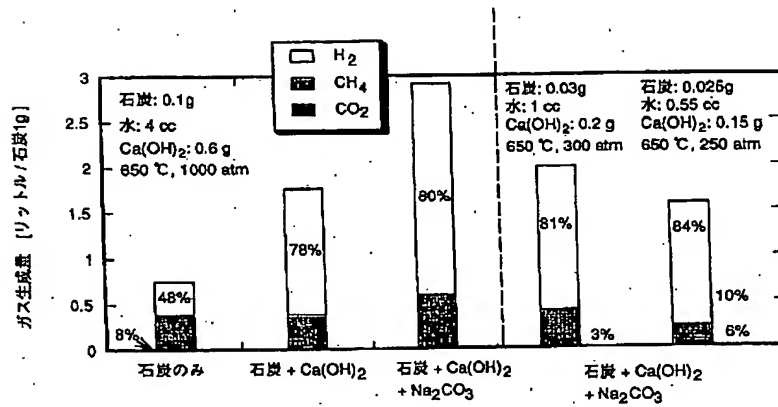
【図5】



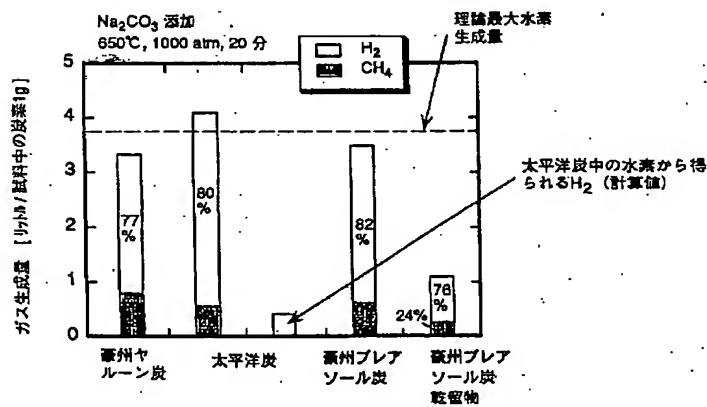
【図2】



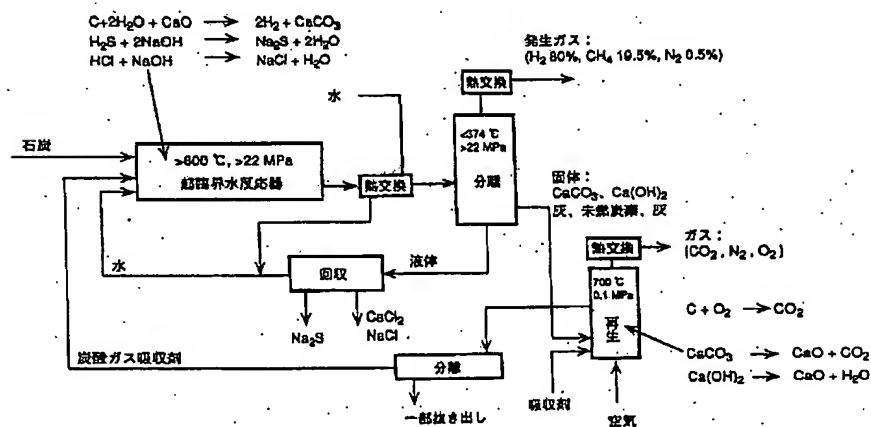
【図3】



【図4】



【図6】



フロントページの続き

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